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Fast Infrared Detection of Cr(CO)₅N₂ in Room-Temperature Solution

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The generation of dinitrogen-substituted transition-metal carbonyl complexes of the general formula $M(CO)_x(N_2)$ has been largely restricted to low-temperature conditions. Ni-$(CO)_3N_2$[1,2] and $Cr(CO)_5N_2$[3] have been synthesized at 10–20 K by the use of matrix isolation methods and more recently by employing pressurized liquid noble gases[4,5] at low temperature as solvents. $Ni(CO)_3N_2$ was found to be thermally unstable at 112 K[4] while $Cr(CO)_5N_2$ was reported to be stable up to 238 K,[5b] the upper limit of the available temperature range. On the other hand, $M(CO)_xN_2$ complexes have scarcely been reported in room-temperature solutions. Conventional flash photolysis studies have implicated $Cr(CO)_5N_2$ as a possible transient in the solution photochemistry of Cr-$(CO)_6$ in hydrocarbon[6] and perfluoro solvents[7] containing dinitrogen. In both cases a transient absorption at 370 nm was assigned to $Cr(CO)_5N_2$, consistent with the low-temperature data.[3,5b]

We have previously shown[8] how, at room temperature, flash photolysis with infrared detection can give important information not accessible from the UV–visible counterpart. In addition to kinetic data, valuable structural information can be gained from the frequency and intensity of the infrared bands associated with a particular transient. With regard to transition metal carbonyls the CO stretching region is often a direct reflection of the geometry of the molecule itself.

The photochemistry of $Cr(CO)_6$ is still not fully understood,[9] but CO detachment is known to occur with the resultant formation of a highly reactive $Cr(CO)_5$ species. This coordinatively unsaturated molecule will readily react with numerous ligands to form $Cr(CO)_5L$ derivatives either as labile species[8,10] or as stable products.[11]

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Table I. Transient Infrared Absorptions (cm^{-1}) of $Cr(CO)_5N_2$ at Various Temperatures and in Various Media

medium	T, K	$\nu_e(CO)$	$\nu_{a_1}(CO)$	$\nu_{a_1}(NN)$	¹³CO satellite	ref
			absorptions and assignments			
cyclo-hexane	~293[a]	1976[b]	1966,[b] 2086[c]	2240[d]	1946[c]	this work[e]
liquid xenon	194	1975.5	1966.8, 2087.0	2237.2		ref 5
CH₄/N₂ matrix	20	1978.2	1959.5,[f] 2086[f]	2240.6[f]		ref 3

[a] Room temperature. [b] Slit width 0.5 mm. [c] Slit width 1.25 mm. [d] Slit width 5 mm. [e] Reproducibility ±2 cm^{-1} or better. [f] Raman band.

Using our technique of flash photolysis with infrared detection,[8] we have now studied the reaction of $Cr(CO)_5$ with dinitrogen, and we report on the identification and behavior of $Cr(CO)_5N_2$ in cyclohexane solution at room temperature.

Experimental Section

The instrumental design of the flash photolysis with infrared detection setup has been described previously.[8] In this study the HgCdTe detector was used throughout. A xenon flash lamp (Xenon Corp., 50 J/pulse, 90% discharge within 5 μs) was used as the exciting light source. The lamp and the associated power supply were securely housed in copper shielding to prevent electromagnetic interference from the flash.

Materials. $Cr(CO)_6$ was purchased from Merck (z. S.) and N₂ (99.9995%) from L'Air Liquide. Cyclohexane (Merck, z. A.) was distilled under argon in a column of 3-m length and 25-mm internal diameter filled with Wilson spirals of 2-mm diameter (80–100 theoretical plates); its purity was checked by gas chromatography and UV spectroscopy. Impurity peaks detectable by gas chromatography were <0.2 ppm. $Cr(CO)_5(¹³CO)$ was prepared from the thermal reaction of (η^2-cis-cyclooctene)$Cr(CO)_5$ with ¹³CO and identified by mass and infrared spectroscopy.[12]

Sample Preparation. We have previously been concerned[8] that flushing solutions even with high-purity gases could over a period of time accumulate impurities. The sampling equipment was therefore modified according to suggestions by Kelly et al.[7,10] A glass vessel, prefilled with N₂, fitted with greaseless taps was used to hold the sample solution. The solvent, cyclohexane, was vacuum degassed prior to the addition of $Cr(CO)_6$. The solution was then degassed by pumping at room temperature, and N₂ gas was added to a pressure of slightly more than 1 atm. The solution was then shaken to ensure saturation with the gas. In this way volatile impurities should be removed, and continuous purging with gas (a possible source for accumulating impurities) was avoided.

In all experiments 10^{-3} M solutions of $Cr(CO)_6$ were used. It was found that it was not necessary to exclude daylight in order to obtain reproducible kinetic and spectral data.
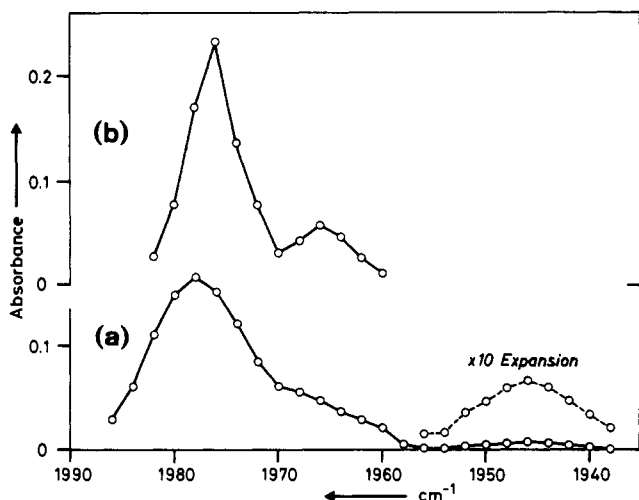
The infrared cell (path length 1 mm) used in these experiments was also evacuable. Circular CaF₂ windows were pressed into a metal casing by indium gaskets, and the cell was connected to the solution vessel by stainless-steel capillary tubing. Thus the entire system was completely closed, and there was no need to flush solutions with gas or to purge the infrared cell. A fresh solution was introduced, normally after about four flashes, into the infrared cell by means of a magnetic solenoid valve. A test series of 16 flashes without changing the solution showed only minimal loss of transient signal.

Results and Discussion

So far, in no flash photolysis study of $Cr(CO)_6$ in cyclohexane has a species been observed prior to the formation of the ubiquitous solvent complex, $Cr(CO)_5C_6H_{12}$. Indeed, it has been shown that this species is already formed within 25 ps of excitation of $Cr(CO)_6$.[13] Not surprisingly, therefore, when a 10^{-3} M solution of $Cr(CO)_6$ in cyclohexane saturated with

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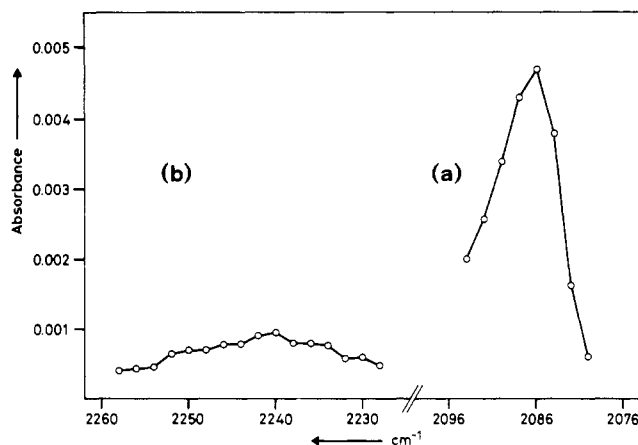(13) Welch, J. A.; Peters, K. S.; Vaida, V. J. Phys. Chem. 1982, 86, 1941.

Figure 1. Low-frequency CO stretching region of the transient spectrum of $Cr(CO)_5N_2$ in N_2-saturated cyclohexane. (a) Spectrum recorded with a slit width of 1.25 mm; up to four sweeps per point measured. Dotted line shows 1946-cm^{-1} band on ×10 expansion. (b) Spectrum recorded with a slit width of 0.5 mm; four sweeps averaged per point measured. See also ref 14.

Figure 2. High-frequency vibrations of the transient spectrum of $Cr(CO)_5N_2$ in N_2-saturated cyclohexane. (a) $\nu_{a_1}(CO)$ recorded with a slit width of 1.25 mm; four sweeps per point measured. (b) $\nu_{a_1}(NN)$ recorded with a 5-mm slit width; 16 sweeps per point measured.

Figure 3. Transient infrared spectrum of $Cr(CO)_4(^{13}CO)N_2$ in N_2-saturated cyclohexane; slit width 1.25 mm; one sweep per point measured (notice the high intensity of the 1946-cm^{-1} absorption compared to that in Figure 1a).

N_2 was flashed, the first transient spectrum observed could readily be attributed to $Cr(CO)_5C_6H_{12}$.

The decay of this solvent complex could be accurately monitored at its maximum absorption (1960 cm^{-1}).[8] $Cr(CO)_5C_6H_{12}$ disappeared under an N_2 atmosphere with a first-order rate constant in the range of 18 000 s^{-1}, i.e., close to the value of 21 000 s^{-1} reported in CO-flushed solutions.[8] Concurrent with the disappearance of $Cr(CO)_5C_6H_{12}$, five new bands grew in (see Table I). These five bands all obeyed the same kinetics, and moreover, they are only observed in solutions containing N_2.

Figure 1a shows the low-frequency CO stretching region of the transient spectrum of this new species recorded with a slit width of 1.25 mm (approximately 7-cm^{-1} resolution). There is clearly a strong feature around 1978 cm^{-1} and a much weaker band at 1946 cm^{-1}. The shape of the 1978-cm^{-1} band suggests that it is not a single absorption. Indeed, when the spectrum was recorded with a slit width of 0.5 mm (see Figure 1b), two bands were clearly resolvable with maxima at 1976 and 1966 cm^{-1}.[14] Owing to the unfavorably low light intensity under this narrow slit, four sweeps had to be averaged per point in order to obtain a reliable spectrum. From the data listed in Table I, it would seem reasonable that these bands be assigned respectively to the e and low-frequency a_1 vibrations of $Cr(CO)_5N_2$. The assignment of the weak band at 1946 cm^{-1}, which was scarcely observed with the narrow slit, is considered later.

A further question to be discussed concerns the high-frequency absorptions expected for $Cr(CO)_5N_2$, $\nu_{a_1}(CO)$ and $\nu_{a_1}(N_2)$. The high-frequency $\nu_{a_1}(CO)$ vibrations were not observed for the species $Cr(CO)_5C_6H_{12}$ and $Cr(CO)_5L$ in the previous study,[8] presumably because of their inherent weakness. However, in the case of $Cr(CO)_5N_2$, low-temperature spectra[3,5] suggest that the intensity ratio ν_{a_1}(high freq)/ν_{a_1}(low
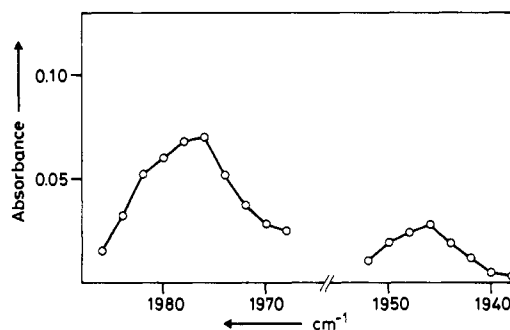
freq) is increased to about 1/6, significantly higher than the value commonly observed for $M(CO)_5$ species. Indeed, we had no problem in observing this vibration (see Figure 2a), particularly in view of the fact that the transparency of cyclohexane is high in this region. The absorption is centered at 2086 cm^{-1}, in agreement with the published low-temperature data (see Table I).

The definitive identification of $Cr(CO)_5N_2$ rests in the observation of the N–N stretching frequency. This absorption is reported to be similar in intensity to that of the high-frequency $\nu_{a_1}(CO)$ vibration.[5] Unfortunately, it occurs in a region where the transmission properties of the solvent cyclohexane are particularly poor. It was scarcely observable at the normal slit width of 1.25 mm. However, measurements (inasmuch as they were possible) at this slit width gave an absorbance similar to that of the high-frequency $\nu_{a_1}(CO)$ vibration. When a slit width of 5 mm was used, a maximum could be traced reproducibly at 2240 cm^{-1} (Figure 2b). This absorption again correlates with the literature values (see Table I). Of course, under lower resolution, the N–N stretching vibration loses amplitude and becomes broader.

The infrared transient spectrum of $Cr(CO)_5N_2$ in room-temperature solution is fully consistent with the low-temperature data. In addition, the weak band at 1946 cm^{-1} (Figure 1) apparently belongs to $Cr(CO)_5N_2$ as well since it obeyed the same kinetics. This band is in the expected position for a ^{13}CO satellite of $Cr(CO)_5N_2$. Moreover, its relative intensity is consistent with this assignment. In order to obtain further information, we also included in our study $Cr(CO)_5(^{13}CO)$.[12] Although the system was still in principle chemically reversible, the degree of isotopic labeling of regenerated chromium hexacarbonyl could no longer be maintained. Therefore, the

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(14) In Figure 1 there is an apparent shift in the maximum absorption from 1978 cm^{-1} (Figure 1a) to 1976 cm^{-1} (Figure 1b). In the former case, where the optical resolution is greater than the fwhm of the CO stretching absorptions, a reliable maximum is necessarily difficult to determine (the measured points at 1980, 1978, and 1976 cm^{-1} have similar absorbance values). Furthermore, the uncertainty in the measured frequencies is about 2 cm^{-1} with the monochromator used,[8] and thus the shift in the maximum absorption is within the experimental error. Conversely, this shift was quite reproducible, which may suggest a small uncertainty associated with the changing of the monochromator slits.
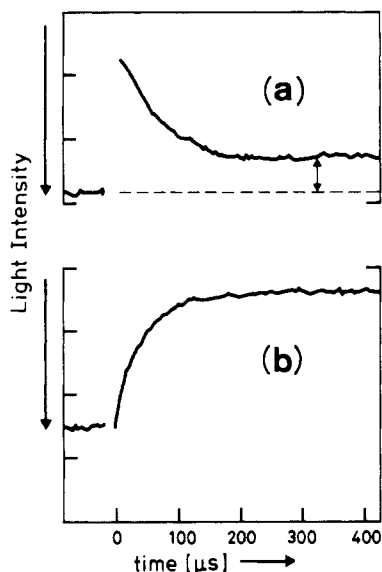
Figure 4. (a) Plot of the decay of $Cr(CO)_5C_6H_{12}$ [$\nu_e(CO)$ at 1962 cm^{-1}]. (b) Plot of the concurrent appearance of the $Cr(CO)_5N_2$ band [$\nu_e(CO)$ at 1976 cm^{-1}]. The vertical double arrow in part a represents the residual absorption at 1962 cm^{-1} of the low frequency $\nu_{a_1}(CO)$ vibration of $Cr(CO)_5N_2$. Both traces are recorded in N_2-saturated cyclohexane with a slit width of 1.25 mm, gain 2000, and one sweep.

solution in the cell necessarily had to be renewed for each flash. Figure 3 shows the result of such an experiment. A considerable increase can be seen in the intensity of the 1946-cm^{-1} absorption.

Although these observations are fully consistent with the assignment of this band to the ^{13}CO satellite of $Cr(CO)_5N_2$, we cannot strictly neglect the further possibility that another product may also be contributing to this absorption. We have preliminary evidence from other experiments that a species presumed to be $Cr_2(CO)_{11}$ also absorbs at ca. 1946 cm^{-1}.[15] It is possible that the band at 1946 cm^{-1} in Figures 1 and 3 is a superposition of the ^{13}CO satellite of $Cr(CO)_5N_2$ and a small quantity of this other species. This would imply that the latter, under these conditions, fortuitously decays with a rate constant similar to that of $Cr(CO)_5N_2$.

A small amount of a further species was also formed with absorptions at 1946 and 1916 cm^{-1}, which can be attributed to a complex, $Cr(CO)_5X$, originating from an unknown impurity. This species, however, decayed much faster with a first-order rate constant of ca. 700 s^{-1}. It was thus easily distinguishable kinetically from the 1946-cm^{-1} absorption of $Cr(CO)_5N_2$. It should be mentioned that Kelly et al.[10] also reported an impurity complex decaying by similar kinetics in CO-flushed solutions. In fact, we have now observed, in a CO-flushed solution with added H_2O, a prominent transient spectrum with the above maxima decaying with a rate constant of 125 s^{-1} (296 K). This would be consistent with the assignment of X to H_2O, which is known to complex with $Cr(CO)_5$.[5b,15]

From the data in Table I and Figures 1 and 2 it is clear that $Cr(CO)_5N_2$ is fully identified from its infrared spectrum. As mentioned above, it was formed with the same rate constant, 18 000 s^{-1}, with which the solvent complex, $Cr(CO)_5C_6H_{12}$, disappeared. This correlation is illustrated in Figure 4, which shows the decay of the 1962-cm^{-1} absorption of $Cr(CO)_5C_6H_{12}$ together with the appearance of the 1976-cm^{-1} band of $Cr(CO)_5N_2$. A detailed mechanistic scheme cannot yet be discussed in full. However, we do have an indication of the stability of $Cr(CO)_5N_2$ in N_2-saturated cyclohexane solutions.
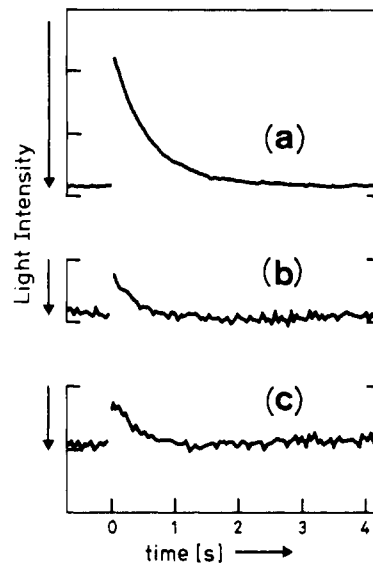
Figure 5. Plot of the decay of $Cr(CO)_5N_2$ in N_2-saturated cyclohexane: (a) monitored at 1978 cm^{-1}, slit width 1.25 mm, gain 2000, one sweep; (b) monitored at 2086 cm^{-1}, slit width 1.25 mm, gain 20 000, four sweeps averaged; (c) monitored at 2240 cm^{-1}, slit width 5 mm, gain 50 000, 16 sweeps averaged.

Figure 5a shows the decay of $Cr(CO)_5N_2$ monitored at 1978 cm^{-1}. The S/N ratio is very high, and one sweep is sufficient to determine the rate constant, 1.7 s^{-1}. $Cr(CO)_5N_2$ is thus quite stable, even at room temperature, under our conditions. The high-frequency $\nu_{a_1}(CO)$ vibration is necessarily more difficult to monitor. Therefore, four sweeps on a higher gain were required to give a satisfactory S/N ratio (Figure 5b). The rate constant determined from this trace is of course less accurate, but nevertheless it agrees well with the value of 1.7 s^{-1}. For reasons described above, the N≡N stretching vibration was even more difficult to observe. Indeed, no reliable kinetic data could be obtained by using a slit width of 1.25 mm regardless of the number of sweeps averaged. Despite these difficulties, a similar rate constant could be derived when the S/N ratio was improved by using a slit width of 5 mm (Figure 5c).

The fate of $Cr(CO)_5N_2$ is not yet known. A simple bimolecular reaction with CO to re-form $Cr(CO)_6$ is unlikely since the observed decay clearly followed first-order kinetics. This would be in agreement with a simple dissociation into $Cr(CO)_5$ and N_2 as the first and rate-determining step, although a more complex mechanism giving rise to pseudo-first-order kinetics must also be considered.[16]
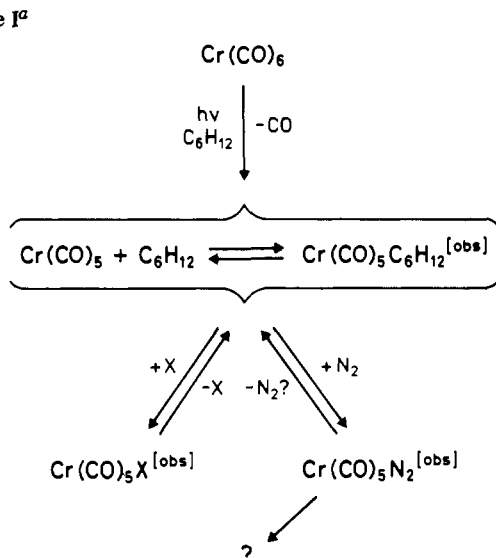
The results of our observations are summarized in Scheme I. As noted at the beginning of this section, the "naked" $Cr(CO)_5$ has not been observed directly in cyclohexane. However, it is reasonable to assume an equilibrium with the solvent complex as shown since $Cr(CO)_5$ has been detected as a precursor to $Cr(CO)_5C_6H_{12}$ by nanosecond spectroscopy at room temperature.[7] The formation of $Cr(CO)_5N_2$ in cyclohexane is slower than from $Cr(CO)_5$ in a noncoordinating solvent by a factor of ca. 10^3.[7] This suggests that the concentration of $Cr(CO)_5$ would have to be on the order of 0.1% under our present conditions.

Conclusion and Outlook

The characterization of transients generated in the solution photochemistry of $Cr(CO)_6$ at room temperature in the previous[8] and present studies amply demonstrates how valuable

(15) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K., unpublished results.

(16) A forthcoming more detailed kinetic analysis, including experiments with varying mixtures of N_2 and CO, should give further insight into the reaction mechanism. Similar experiments proved invaluable in the kinetic analysis of $Ni(CO)_3N_2$ in liquid krypton.[4]

Scheme I[a]

Cr(CO)₆

$$\downarrow \begin{array}{c} h\nu \\ C_6H_{12} \end{array} \; -CO$$

$$\overbrace{\qquad\qquad\qquad\qquad\qquad\qquad}$$

Cr(CO)₅ + C₆H₁₂ $\rightleftharpoons$ Cr(CO)₅C₆H₁₂[obs]

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad}$$

+X ╱ ╲ ╱ ╲ +N₂
-X   -N₂?

Cr(CO)₅X[obs]   Cr(CO)₅N₂[obs]

?

[a] [obs] = transient observed; X = unknown trace impurity. Note that reaction with N₂ is much more important than with X under our conditions.

the technique of flash photolysis with infrared detection has become. Notably in the case of $Cr(CO)_5N_2$, a detailed infrared study in room-temperature solution (q.v.) can now be directly compared with low-temperature work[3,5] (see Table I). The opportunity for such a comparison is rarely possible. There is clearly a scope for a wide range of applications of solution flash photolysis with infrared detection.[17]

The unique use of the specifically monolabeled compound $Cr(CO)_5(^{13}CO)$, the synthesis of which has recently been accomplished in our laboratory,[12] proved valuable in the interpretation of the infrared spectrum of $Cr(CO)_5N_2$. More extensive ^{13}CO isotopic studies of $Cr(CO)_5$ species using this compound should now also be possible.

Acknowledgment. We thank Dr. M. Poliakoff for valuable discussions, V. Skibbe for preparing the sample of Cr(C-O)₅(¹³CO), and K. Sandmann for able technical assistance.

(17) Other obvious and important targets of flash photolysis with infrared detection are thermally equilibrated excited states. The short lifetimes and, in the case of other than metal carbonyl compounds, considerably weaker absorptions demand improvements in sensitivity and time resolution such as are in preparation, including pulsed laser excitation and laser diode infrared sources. An interesting alternative to our approach, albeit restricted as yet to the long nanosecond to microsecond time scale, has recently been presented. The pulsed continuum infrared radiation of a laser-produced plasma is used as an extraordinarily powerful source (Adamson, A. W.; Cimolino, M. C. *J. Phys. Chem.* **1984,** *88,* 488). We thank Professor Adamson for the communication prior to publication.

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Hyperfine Parameters in an Exchange-Coupled Copper(II)–Nickel(II) Pair. Relation to the Local Hyperfine Splitting

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Heterobimetallic systems are particularly interesting in the theory of exchange interactions. They provide the possibility
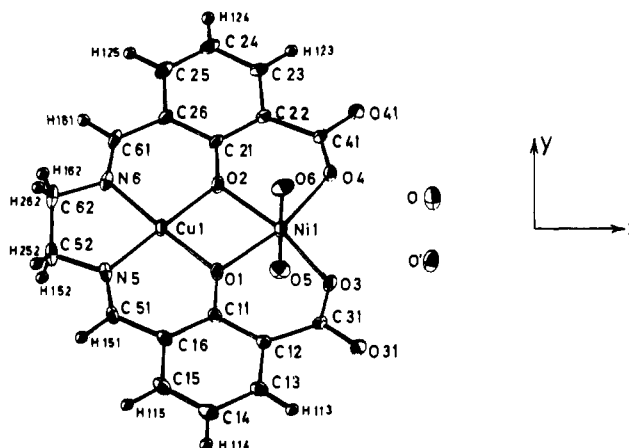

Figure 1. Perspective view of [CuNi], with the *x* and *y* molecular axes (from ref 8).

of comparing spin-Hamiltonian parameters for each pair state with the local parameters associated with the single-ion ground states.[2–7,11]

To obtain all the expected information, it is necessary to have at one's disposal the pure material for the magnetic susceptibility study and a host material doped with the coupled system for the observation of hyperfine structure in the EPR spectrum. To our knowledge, till now, these two conditions were not fulfilled for any heterobimetallic system. The host lattice must present two characteristics: to be isostructural with the pure material and to be EPR silent in the temperature range where the spectra are recorded. We had previously investigated the complex CuNi(fsa)₂en(H₂O)₂·H₂O, noted [CuNi], where (fsa)₂en⁴⁻ is the bichelating ligand derived from the Schiff base 1,2-bis[(2-hydroxy-3-carboxybenzylidene)-amino]ethane.[8] Magnetic and EPR properties were compared to those of the isostructural [CuMg] and [NiNi] complexes, in which only one of the two metal ions is paramagnetic. We determined the energy gap $-3J/2 = 213 \text{ cm}^{-1}$ between the doublet and quartet states arising from the antiferromagnetic coupling. We found quite a satisfying agreement between the observed *g* values of the ground doublet state of [CuNi] and those calculated from the *g* values of the noncoupled [CuMg] and [NiNi] compounds.

Since we worked with pure materials, we were not able to carry out the same investigation for the hyperfine tensors. However, [CuNi] is potentially a good candidate for checking the validity of similar relations between pair and local hyperfine parameters. Such an investigation became possible when we realized that [CuCo] was an ideal host lattice for this purpose. [CuCo],[9] [CuNi], and [CuMg],[10] have identical trigonal structures with three molecules per unit cell. The structure of one of these compounds, namely [CuNi], is recalled in Figure 1, with the in-plane *x* and *y* molecular axes. The *z* molecular axis is collinear with the *c* trigonal axis.

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